Inorg. Chem. **2002**, *41*, 219–228

Activation of Organonitriles toward β-Electrophilic Attack. Synthesis and Characterization of Methyleneamide (Azavinylidene) Complexes of Rhenium

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Received August 6, 2001

Treatment of the nitrile complexes *cis*-[ReCl(NCR)(dppe)$_2$] (R = aryl; dppe = $Ph_2PCH_2CH_2PPh_2$) with [Et_2OH][BF_4] or $SiMe_3CF_3SO_3$ in CH_2Cl_2 led to the formation of the methyleneamide (alkylideneamide or azavinylidene) compounds *cis*-[ReCl{NC(E)C_6H_4X-4}(dppe)$_2$]Y [E = H; X = OMe (**1b**), Me (**1c**), H (**1d**), F (**1e**), or Cl (**1f**), Y = BF_4; E = $SiMe_3$, X = Me (**1c′**), Y = CF_3SO_3] and *trans*-[ReCl{NC(H)C_6H_4X-4}(dppe)$_2$][BF_4] [X = NEt_2 (**2a**), OMe (**2b**), H (**2d**), F (**2e**), or Cl (**2f**)]. They were characterized by multinuclear NMR spectrometry and X-ray crystallography (**2e**) which shows that the methyleneamide ligand exhibits linear (three-electron donor) geometry and behaves as a strong π-electron acceptor. The complex $^{31}P\{^1H\}$ and ^1H [NC(*H*)C_6H_4X-4] NMR patterns for the cis isomers were analyzed as ABCD and ABCDX (X part) spin systems, respectively. Complexes **1** and **2** undergo deprotonation by base to form the trans isomers of the corresponding nitrile complexes, *trans*-[ReCl(NCC_6H_4X-4)(dppe)$_2$] [X = NEt_2 (**3a**), OMe (**3b**), H (**3d**), F (**3e**), or Cl (**3f**)] whose spectroscopic data are also presented and which on protonation give the corresponding trans isomers of the methyleneamide complexes (**2**). Reactions of *cis*-[ReCl(NCR)(dppe)$_2$] with [Et_3O][PF_6] resulted in their oxidation and isomerization to afford *trans*-[ReCl(NCC_6H_4X-4)(dppe)$_2$][PF_6] [X = Me (**4c**), H (**4d**), or Cl (**4f**)].

Introduction

Dinitrogen complexes can constitute a potential source of electron-rich transition metal centers suitable for activation of a variety of unsaturated-N or -C small molecules, namely, those related to N_2.[1] Hence, e.g., isocyanides,[2] alkynes,[3] phosphaalkynes,[4] nitric oxide,[5] cyanide,[6] and organonitriles[7−9] can bind such metal sites and undergo activation toward electrophilic attack, reduction, or rearrangement reactions which normally can be accounted for by the electronic and structural properties of those binding centers.

In particular isocyanides[10] and organonitriles,[11,12] whose rich coordination chemistry (comprising activation toward

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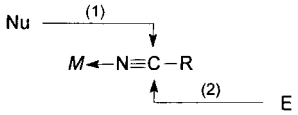
10.1021/ic010841m CCC: $22.00
Published on Web 01/03/2002

Scheme 1



nucleophiles, insertion reactions, etc.) has been developed at metal centers in higher oxidation states when they can undergo typically nucleophilic additions at the unsaturated carbon atom (reaction 1, Scheme 1, for organonitriles, Nu = Nucleophile), can become susceptible to ready β-protonation (reaction 2, Scheme 1, for organonitriles, E = electrophile = H^+) when binding a suitable low-valent and strong π-electron-releasing metal site, to afford the corresponding aminocarbyne (CNHR)[2] or methyleneamide (NCHR, also called alkylideneamide or azavinylidene)[7−9] species. Our preliminary report[7] on β-protonation of an organonitrile, at [ReCl(NCR)(dppe)$_2$] (R = aryl, dppe = $Ph_2PCH_2CH_2PPh_2$), constituted a novel and convenient route for the latter type of ligands (NCHR) which were, and still are, usually obtained[13−17] by quite different methods.

In view of the synthetic significance of methyleneamide ligands, e.g., toward ligating imines,[15] imides,[9,14h,i,18] amines,[15,19] and nitriles,[15b] the above route should be further explored. The involvement of the β-protonation route was postulated[1b] in the nitrogenase reduction of organonitriles to ammonia and alkanes and was proposed[18] in the protic conversion of organonitriles into the imido complexes [Re(NCH$_2$R)X$_3$(dppbe)] [R = alkyl, X = Cl or Br, dppbe = 1,2-bis(diphenylphosphino)benzene]. Recently it was extended by others[9] to *trans*-[M(N$_2$)(NCR)(dppe)$_2$] (M = Mo or W) by achieving their further conversion into imido derivatives, *trans*-[MX(NCH$_2$R)(dppe)$_2$]$^+$ (X = halide), or even metal nitrides, *trans*-[Mo(N)(NCCHCOR)],[9a] formed upon complete N≡C triple bond protic cleavage at β-ketonitriles (e.g., N≡CCH$_2$COR), in *trans*-[Mo(N$_2$)(N≡CCH$_2$COR)(dppe)$_2$], with concomitant liberation of the corresponding vinyl ketones CH$_2$=CHCOR.

Therefore, a promising and novel coordination chemistry of nitriles, based on their activation toward electrophiles, seems starting to emerge and prompted us to describe in detail our own studies at the electron-rich {ReCl(dppe)$_2$} site, which show that aromatic nitriles at *cis*- or *trans*-[ReCl(NCR)(dppe)$_2$] undergo stereoselective β-protonation (by HBF_4) or β-silylation (by $SiMe_3CF_3SO_3$) to give *cis*- or *trans*-[ReCl{NC(E)R}(dppe)$_2$]$^+$ (E = H or $SiMe_3$). Hence, the present study concerns the still underdeveloped mode of

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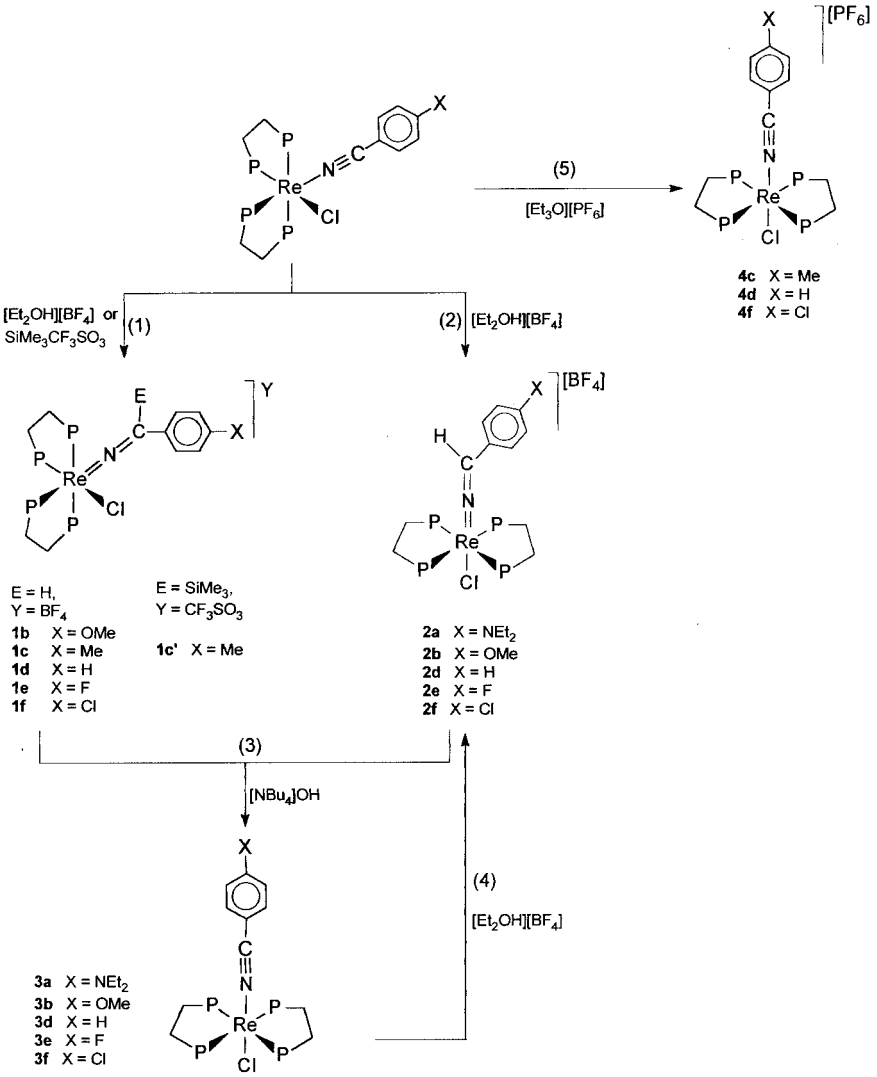
Scheme 2



nitrile activation toward electrophiles (reaction 2, Scheme 1) and, to our knowledge, provides the first example of addition of an electrophile other than the proton. No final hydride products were obtained, and the complexes which, in a preliminary study,[8,20] were proposed as $[ReCl(H)(NCR)(dppe)_2][BF_4]$ are now reformulated as the trans isomers of the methyleneamide complexes, i.e., *trans*-$[ReCl(NCHR)(dppe)_2][BF_4]$ as demonstrated (see below) by detailed NMR studies and by an X-ray diffraction analysis. This reformulation does not invalidate those preliminary studies, provided it is considered therein. The use of $[Et_3O][PF_6]$ as the electrophile resulted in the oxidation of the metal to give the Re^{II} nitrile complexes *trans*-$[ReCl(NCR)(dppe_2][PF_6]$. Both isomers of the methyleneamide complexes undergo deprotonation by base affording exclusively the trans isomers of the parent nitrile complexes (thus providing an improved method for their preparation), and the detailed syntheses and spectroscopic properties (including simulations of $^{31}P\{^1H\}$ and ^1H NMR data) of the methyleneamide (both isomers) and nitrile (trans isomers) complexes are also now presented.

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Results and Discussion

Methyleneamide Complexes. Treatment of CH_2Cl_2 solutions of *cis*-$[ReCl(NCR)(dppe)_2]$ (R = aryl) with $[Et_2OH][BF_4]$ or $SiMe_3CF_3SO_3$ resulted (reactions 1 and 2, Scheme 2) in the formation of the methyleneamide complexes *cis*-$[ReCl\{NC(E)C_6H_4X\text{-}4\}(dppe)_2]Y$ [E = H, X = OMe (**1b**, already reported[7] in a preliminary way), Me (**1c**), H (**1d**), F (**1e**), or Cl (**1f**), Y = BF_4; E = $SiMe_3$, X = Me (**1c′**), Y = CF_3SO_3] and *trans*-$[ReCl\{NC(H)C_6H_4X\text{-}4\}(dppe)_2][BF_4]$ [X = NEt_2 (**2a**), OMe (**2b**), H (**2d**), F (**2e**), or Cl (**2f**)]. The pure isomeric forms were isolated in moderate yields (ca. 30−60%) depending on the substituent (X) of the phenyl ring (electron-donor groups favor the cis isomers, whereas electron acceptors promote the formation of the trans ones). Side and decomposition products such as *trans*-$[ReCl_2(dppe)_2]^n$ (n = 0 or 1)[21] or the corresponding dinitrile complexes *cis*-$[Re(NCR)_2(dppe)_2][BF_4]$[22] were also isolated on working up the reaction solutions.

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The trans isomers **2** can be obtained in nearly quantitative yields by using, as starting materials, the trans isomers of the nitrile complexes, *trans*-[ReCl(NC$_6$H$_4$X-4)(dppe)$_2$] (**3**, see below), which also undergo fast protonation by HBF$_4$ (reaction 4, Scheme 2) and, in contrast with the cis isomers, form exclusively the trans methyleneamide products.

The activation of the organonitriles toward protonation or silylation can be rationalized in terms of the high π-electron-releasing ability of their electron-rich Re^{I} binding center, {ReCl(dppe)$_2$}. In fact, in both *cis*- and *trans*-[ReCl(NC$_6$H$_4$X-4)(dppe)$_2$], the nitrile ligands exhibit, in the IR spectra, ν(N≡C) at significantly lower wavenumbers than in the corresponding free ligands [for the *cis* isomers, the shift $\Delta\nu$(NC) on coordination is in the range from −20 (for X = NEt$_2$) to −70 (for X = F) cm^{-1},[23] and for the trans isomers, see below, the shift is even more pronounced], indicating an extensive π-electron acceptance of such ligands. This is also consistent with the unusually short Re−N bond, 1.978(5) Å, observed[24] for the acetonitrile complex *trans*-[ReCl(NCMe)(dppe)$_2$]. The electrophilic attack occurs exclusively at the β-position (the C atom) as observed for isocyanides (CNR),[2] vinylidenes,[3b,c] and allene[3a,e,f] ligands when binding the same metal center. No further electrophilic addition occurs in contrast with the above-mentioned *trans*-[M(N$_2$)(NCR)(dppe)$_2$] (M = Mo or W) complexes[9] in which replacement of the labile N$_2$ by an effective electron-donor anionic ligand promotes a second protonation at the methyleneamide group to give a ligated imido species.

The unambiguous formation of a methyleneamide species has been proved by the single-crystal X-ray diffraction analysis of *trans*-[ReCl{NC(H)C$_6$H$_4$F-4}(dppe)$_2$][BF$_4$] **2e**, and clear evidence for the NC(H)R ligand, in both cis and trans isomers (series of complexes **1** and **2**), has been provided by NMR spectrometry (see below).

The molecular structure of **2e** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1.

The structural data for the methyleneamide ligand indicate that it approaches more the linear coordination mode (three-electron donor) (a) than the bent one (single-electron donor) (b), thus conferring the 18-electron configuration to the complex.

(*a*) (*b*)

In fact, the Re−N distance, 1.831(8) Å, is consistent with a significant double-bond character of this bond, being shorter than those observed in the rhenium complexes *trans*-[ReCl(NCMe)(dppe)$_2$] [1.978(5) Å],[24] *cis*- or *trans*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$]$^+$ [average 2.07(2) or 2.063(7) Å, respectively],[25,26] or even the related *trans*-[Re(OH)(NCMe$_2$)(dppe)$_2$][HSO$_4$] [1.901(5) Å][27] with a linearly coordinated

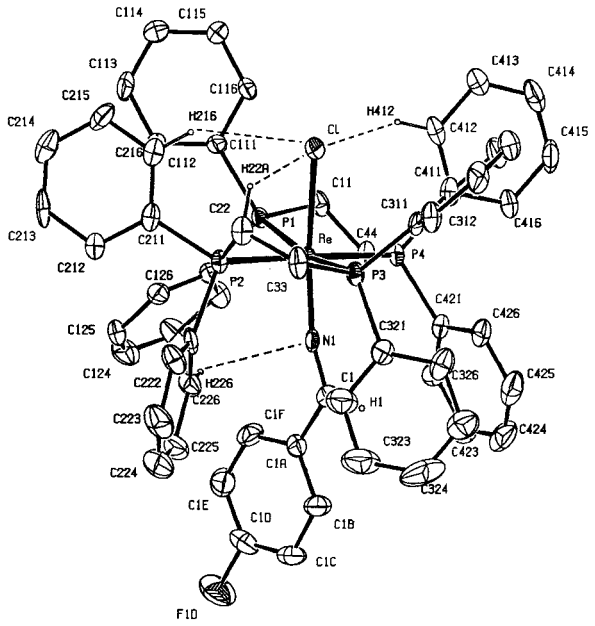

Figure 1. Molecular structure of the complex cation in *trans*-[ReCl{NC(H)C$_6$H$_4$F-4}(dppe)$_2$][BF$_4$] **2e**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[ReCl{NC(H)C$_6$H$_4$F-4}(dppe)$_2$][BF$_4$]·CH$_2$Cl$_2$

Re−N(1)	1.831(8)	Re−N(1)−C(1)	165.7(10)
N(1)−C(1)	1.244(15)	N(1)−C(1)−C(1A)	127.6(13)
C(1)−C(1A)	1.498(16)	N(1)−Re−Cl	171.8(3)
Re−Cl	2.437(3)	N(1)−Re−P(1)	100.1(3)
Re−P(1)	2.487(3)	N(1)−Re−P(2)	97.0(3)
Re−P(2)	2.436(3)	N(1)−Re−P(3)	91.2(3)
Re−P(3)	2.480(3)	N(1)−Re−P(4)	81.4(3)
Re−P(4)	2.475(3)	Cl−Re−P(1)	87.57(9)
		Cl−Re−P(2)	84.56(9)
		Cl−Re−P(3)	81.11(9)
		Cl−Re−P(4)	97.27(9)
	Hydrogen Bonding		
H(22A)···Cl	2.7915	C(22)−H(22A)···Cl	115.44
H(216)···Cl	2.7790	C(216)−H(216)···Cl	144.55
H(412)···Cl	2.6365	C(412)−H(412)···Cl	144.78
H(226)···N	2.6124	C(226)−H(226)···N	112.29

methyleneamide. Moreover, the average Re−P distance of **2e** [2.469(3) Å] is identical to that of the latter rhenium compound [2.461(2) Å][27] and of the related aminocarbyne *trans*-[ReCl(CNHMe)(dppe)$_2$][BF$_4$],[28] and the Re−Cl distance of 2.437(3) Å in **2e** is even shorter than that [2.484(6) Å][28] of the aminocarbyne compound, suggesting that the methyleneamide ligand is behaving as an effective π-electron acceptor, as known[29,30] for the ligating CNHMe. This is consistent with the predominance of the trans isomers **2** (with the strong electron-donor chloro ligand in trans position relative to the methyleneamide) relative to the cis isomers

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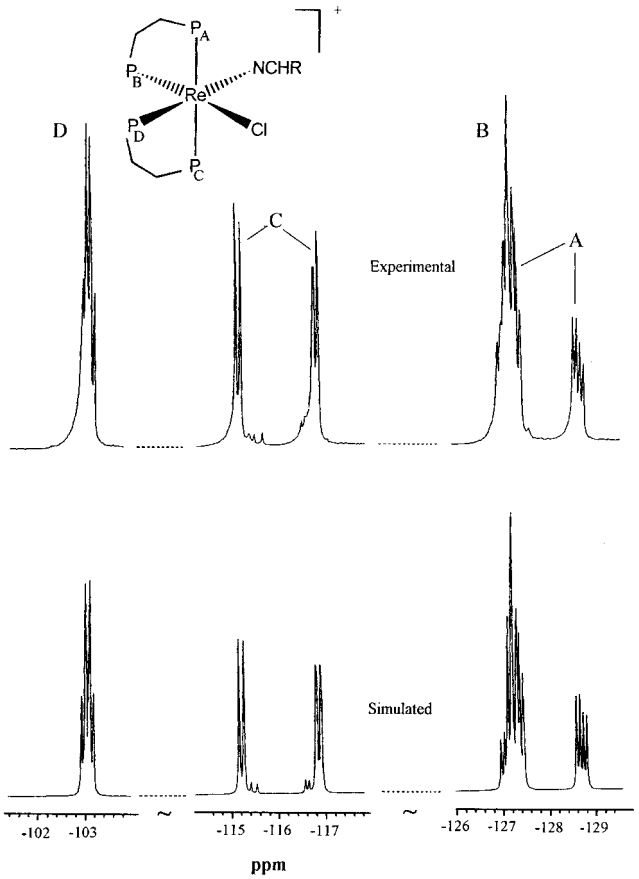

Figure 2. Experimental (CD_2Cl_2) (top) and theoretical (bottom) $^{31}P\{^1H\}$ NMR spectra of *cis*-[ReCl{NC(H)C_6H_4Cl-4}$(dppe)_2$][BF_4] **1f** analyzed as an ABCD spin system (see Experimental Section).

1, for electron-acceptor nitrile substituents (X) which promote the ligand electron-withdrawing ability. The N(1)−C(1) bond distance [1.244(15) Å] is somewhat shorter than the average for C(sp^2)═N(sp^2) (e.g., 1.281 Å in oximes),[31] and the Re−N−C moiety deviates significantly from the linearity [165.7-(10) °] as known for other cases[9a,32] with considered linearly coordinated methyleneamides. The N═CH−R angle of 127.6(13)° is consistent with the expected sp^2 hybridization at the methyleneamide carbon, and it confirms the occurrence of the protonation at the β-carbon atom of the nitrile ligand.

Four intramolecular hydrogen bonds were calculated, involving not only the chloride ligand but also the nitrogen atom, the latter conceivably accounting for the above-mentioned deviation from the linearity of the methyleneamide ligand.

Evidence for the ligating methyleneamide in both sets of complexes **1** and **2** is also given by the ^{13}C-proton coupled NMR spectra which show the expected NC*H*R doublet (J_{CH} ca. 160 Hz) at δ ca. 114−129 (although in a few cases partially buried under the phenyl-carbon resonances) which coalesces into a singlet in the $^{13}C\{^1H\}$ NMR spectra. Moreover, in the ^1H NMR spectra, NOE experiments with irradiation at the NC*H*R resonance (see below) boosted the

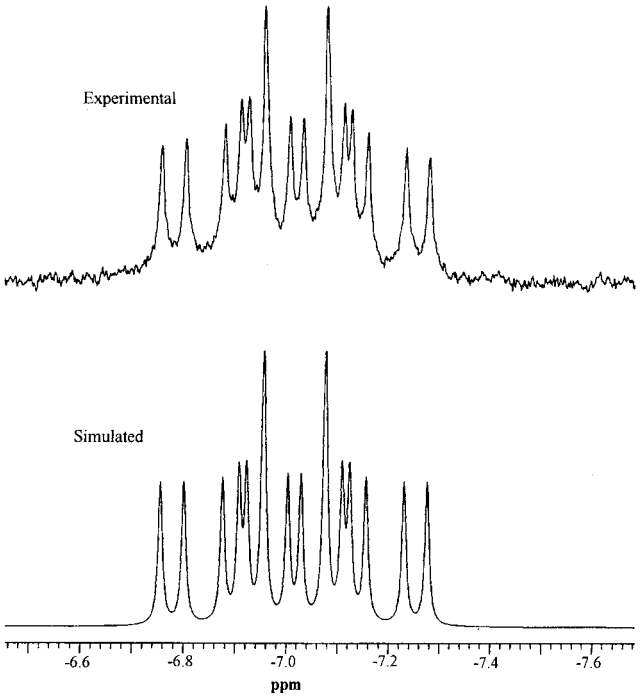

Figure 3. Experimental (CD_2Cl_2) (top) and theoretical (bottom) ^1H NMR spectra (high-field region) of *cis*-[ReCl{NC(H)C_6H_4Cl-4}$(dppe)_2$][BF_4] **1f** analyzed as the X part of an ABCDX spin system (see Experimental Section).

intensity of the ortho protons (H_o) of the phenyl ring in the R group, confirming the closeness of the methyleneamide proton and the latter aromatic protons.

In the $^{31}P\{^1H\}$ NMR spectra, the trans isomers **2** exhibit the expected singlet, whereas for the cis isomers **1** (Figure 2 for **1f**) the spectra show ABCD spin systems (the mutually trans P_A and P_C have the highest J values, and P_D, trans to the methyleneamide ligand, is most affected by the X substituent).

Subsequently, the high-field (δ −6.8 to −7.3) complex pattern (with 14 or 16 lines) of the methyleneamide NC*H*R proton, in the ^1H NMR spectra of complexes **1**, was analyzed as the X part of an ABCDX spin system (Figure 3 for **1f**). It was assumed that P_D, trans to the methyleneamide ligand, couples more effectively to the NC*H*R proton (J_{PH} ca. 60 Hz) than the other P nuclei (J_{PH} ca. 14−16 Hz). For the trans isomers **2**, the NC*H*R resonance appears as a high-field (δ ca. −3.8 to −4.8) quintet ($^4J_{PH}$ 6.1−6.8 Hz), consistent with the equivalence of the four P nuclei. These values of the coupling constant are lower than those reported for $^2J_{PH}$ in hydride−phosphine complexes of rhenium (21−66 Hz range),[33−35] thus confirming the assignment of that resonance to a non-hydride proton, in spite of its high-field chemical shift. A significant shielding of the NC*H*R proton (δ ca. 0.9 to −1.5),[36] although not so pronounced as in our case, was

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also reported for other rhenium−methyleneamide complexes in which this ligand is believed to act as a three-electron donor (linear geometry). However, this NMR behavior is not diagnostic of such a geometry since for other complexes with linear methyleneamides the NC*H*R resonance can be rather deshielded (e.g., δ ca. 8.3−9.4 in some Sc or Zr species).[37]

In the phenyl region, the proton resonances observed upfield from the bulk of the complex multiplet are assigned to the phenyl protons of the methyleneamide ligand (AB-type pattern, for each pair of ortho and adjacent meta protons). For **2e**, the coupling of the methyleneamide−phenyl protons to the fluorine nucleus was observed for the meta (relative to the NC group) protons [apparent triplet resulting from the overlap of a doublet ($^3J_{HH}$) of doublets ($^3J_{HF}$)] and for the ortho protons [doublet ($^3J_{HH}$) of doublets ($^4J_{HF}$)] and confirmed by ^{19}F NMR.

In their IR spectra, complexes **1** and **2** do not exhibit any band which could be assigned to the N═C stretching. A similar situation was found in other methyleneamide compounds such as [$ReCl_2$(NCHR)LL′] (R = Me or Ph; L = py; L′ = monophosphine],[36] although cases are known[36,37] in which such a vibration was detected as a medium to weak band in the 1525−1725 cm^{-1} range. In [Mo(η^5-C_5H_5)L_2{NC(Bu^t)Ph}] (L = CO or PPh_3)[36] it was observed that ν(N═C) was highly dependent on the coligands. In the 550−400 cm^{-1} range the cis isomers present one (or two) strong band(s) whereas the trans ones exhibit several clearly defined medium-intensity bands, in agreement with the previously observed[22,27] typical CC vibration modes of the phenyl rings of the *cis*- and *trans*-diphosphines. The bands due to the counterions are observed in the usual regions.

In the FAB-MS spectra of complexes **1**, the molecular ion is not detected and the fragmentation pathways are generally initiated by the loss of the ligating NCHR, Cl^-, or one of the diphosphines. While in the former case the process is followed by the loss of Cl^- or fragmentation of dppe, in the latter cases the loss of Cl^- or of one dppe precedes the fragmentation of the remaining diphosphine with retention of the rhenium−methyleneamide bond. The fragmentation pattern for these complexes resembles that observed for the corresponding neutral *cis*-mononitrile species.[38] In the trans complexes **2** the molecular ion is clearly detected (in contrast with the less stable cis isomers **1**) and the fragmentation of the diphosphine can occur prior to the loss of NCHR. Fragments derived from the liberation of one dppe and subsequent fragmentation of the remaining one and addition of oxygen from the NOBA matrix are also observed.

Nitrile Complexes with the Trans Geometry. The preparation of the pure trans isomers of the Re^I nitrile complexes **3**, i.e., *trans*-[$ReCl(NCC_6H_4X$-4)(dppe)$_2$] [X = NEt_2 (**3a**), OMe (**3b**), H (**3d**), F (**3e**), or Cl (**3f**)], involves the deprotonation, by [NBu_4]OH, of the methyleneamide compounds **1** or **2** (reaction 3, Scheme 2, with almost quantitative yield), which is a better route than their synthesis from the dinitrogen complex *trans*-[$ReCl(N_2)$(dppe)$_2$], on replacement of N_2 by NCR,[24] which leads to contamination with the cis isomers that are the main products[23] of the reaction.

The oxidized Re^{II} form **4** of those nitrile complexes can be obtained (ca. 70−80% yields) in a more direct way by oxidation of the corresponding Re^I *cis*-nitrile isomers. This can be conveniently carried out by treatment of CH_2Cl_2 solutions of the latter compounds, at low temperature, with [Et_3O][PF_6] (reaction 5, Scheme 2) followed by warming, giving *trans*-[$ReCl(NCC_6H_4X$-4)(dppe)$_2$][PF_6] [X = Me (**4c**),[39] H (**4d**), or Cl (**4f**)]. Hence, although silylation of the organonitrile was observed on the reaction of *cis*-[$ReCl(NCC_6H_4Me$-4)(dppe)$_2$] with $SiMe_3CF_3SO_3$ to give the methyleneamide product *cis*-[ReCl{NC($SiMe_3$)C_6H_4Me-4}(dppe)$_2$]CF_3SO_3 **1c′**, attempted alkylation of the *cis*-nitrile complexes by using the stronger and less bulky [Et_3O][BF_4] electrophile resulted in metal oxidation to form the corresponding Re^{II}−nitrile products **4**.

The cis-to-trans isomerization was promoted by oxidation in agreement with electrochemical studies on *cis*-[$ReCl(NCC_6H_4Me$-4)(dppe)$_2$][39] and on the related *cis*-[Re(NCR)$_2$(dppe)$_2$]$^+$ (R = aryl or alkyl)[40] and *cis*-[ReCl(CO)(dppe)$_2$][27] complexes which were shown to undergo anodically induced isomerization. Electron-transfer-induced structural changes of coordination compounds constitute a matter of current and growing interest.[41,42]

In the IR spectra, the Re^I complexes **3** exhibit ν(N≡C) at wavenumbers (2100−2080 cm^{-1}) that are significantly lower (by ca. 70−90 cm^{-1}) than those of the corresponding cis isomers,[22] indicating a more effective π-electron-releasing ability of the *trans*-{$ReCl(dppe)_2$} binding site relative to the cis one. As expected, the cationic Re^{II} complexes **4** present ν(N≡C) at higher wavenumbers (2130−2120 cm^{-1}). In both series of compounds, the complex IR pattern in the 550−450 cm^{-1} range is diagnostic[22,27] of their trans geometry.

In compounds **3** a broad singlet is observed in the ^{31}P-{^{1}H} NMR spectra, but their instability in solution precluded reliable ^{13}C NMR studies. Complexes **4** display broad NMR spectra due to their paramagnetism.

The FAB-MS spectra of complexes **3** and **4** exhibit fragmentation patterns similar to those of the methyleneamide compounds **2** with the same isomeric form.

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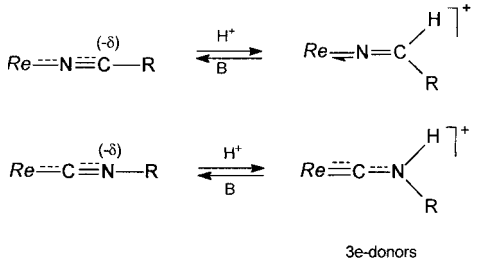
Scheme 3[a]



[a] *Re* = {ReCl(dppe)$_2$}. B = base.

Final Comments

These studies demonstrate that organonitriles are activated by the electron-rich and strong π-electron-releasing {ReCl(dppe)$_2$} site toward ready β-electrophilic addition (which can be reversed by base) to form methyleneamide (or azavinylidene) species, thus following a general pattern of reactivity similar to that exhibited by isocyanides (C≡NR)[2] at the same metal center which leads to aminocarbyne products (CNHR) (Scheme 3 for the case of protonation). As a result of this reaction, a weakening of the unsaturated NC bond occurs with a concomitant strengthening of the metal−ligand bond showing the propensity of rhenium to form multiple bonds to nitrogen and carbon. The derived ligand (NCHR or CNHR) can be considered to behave as a three-electron donor (thus giving the closed-shell configuration to the complexes) and as a strong π-electron acceptor. The ligated methyleneamide thus presents the linear coordination mode and resembles the linearly coordinated nitrosyl (NO^+) which is also believed[43] to act as a three-electron donor and a strong π-electron acceptor at the same rhenium site.

These reactions contrast with the common and much more studied activation of nitriles[11,12] and isocyanides,[10] toward nucleophiles upon coordination to a metal center without a significant π-electron-releasing ability. In particular, the ligated acetonitriles in the Re^{IV} complex *cis*-[ReCl$_4$(NCMe)$_2$] are electrophilically activated toward nucleophilic addition of oximes RR′C═NOH (R, R′ = alkyls) to give the iminoacylated species, or (alkylideneaminooxy)imines, *cis*-[ReCl$_4${NH═C(Me)ON═CRR′}$_2$].[12i]

The reactions of the current study can also involve the geometrical isomerization of the {ReCl(dppe)$_2$} binding site that appears to be determined by a delicate balance of the electron-acceptor/donor properties of the nitrile or methyleneamide ligand, the metal oxidation state, and the particular experimental conditions applied. No seven-coordinate species derived from addition of the electrophile to the metal were detected, but oxidation of this atom can result from reaction with a common strong alkylating agent.

Experimental Section

All the manipulations and reactions were carried out in the absence of air using standard inert-gas flow and vacuum techniques. Solvents were purified by standard procedures, and the series of complexes *cis*-[ReCl(NCC$_6$H$_4$X-4)(dppe)$_2$] (X = NEt$_2$, OMe, Me, H, F, or Cl) were prepared by a published method.[23] Infrared (IR) measurements were carried out in KBr pellets (values in cm^{-1}; intensity of bands is referred to as m = medium, s = strong) on a Perkin-Elmer 683 spectrophotometer and ^{1}H, ^{19}F, ^{31}P, and ^{13}C NMR spectra on a Varian Unity 300 spectrometer. Chemical shifts are in ppm relative to SiMe$_4$ (^{1}H and ^{13}C), CFCl$_3$ (^{19}F), or P(OMe)$_3$ (^{31}P) (s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, br = broad, dm = doublet of multiplets, tm = triplet of multiplets, dd = doublet of doublets, tt = triplet of triplets). The complex NMR spectral analyses were performed by using a LAME iterative program.[44] Mass spectrometric measurements were performed on a Trio 2000 spectrometer, and positive-ion FAB mass spectra (FAB$^+$-MS) were obtained by bombarding 3-nitrobenzyl alcohol (NOBA) matrixes of the samples with 8 keV Xenon atoms. Nominal molecular masses were calculated using the most abundant rhenium isotope, ^{187}Re (63%).

Syntheses of *cis*- and *trans*-[ReCl{NC(H)C$_6$H$_4$X-4}(dppe)$_2$][BF$_4$] [X = NEt$_2$ (2a), OMe (1b and 2b), Me (1c), H (1d and 2d), F (1e and 2e), or Cl (1f and 2f)]. The methyleneamide complexes **1** and **2** were prepared by reactions of the appropriate nitrile complexes *cis*-[ReCl(NCC$_6$H$_4$X-4)(dppe)$_2$] in dichloromethane, with a diethyl ether solution of HBF$_4$ (a 1:11 diluted Et$_2$O solution of 85% [Et$_2$OH][BF$_4$]). The reaction solution was left stirring for 1 h at room temperature and then was concentrated under vacuum. After addition of Et$_2$O the solution was left standing. The first crop of precipitate thus obtained was separated by filtration and was generally a mixture of the methyleneamide complex **1** with side products, in particular *trans*-[ReCl$_2$(dppe)$_2$]^n (n = 0 or 1) [21] and/or *cis*-[Re(NCC$_6$H$_4$X)$_2$(dppe)$_2$]$^+$.[22] When isolation of complex **1** from the contaminants could not be achieved mechanically, recrystallization from CH$_2$Cl$_2$/Et$_2$O was carried out (yield ca. 30−40% for the pure isomer). New crops, containing the corresponding methyleneamide complex **2**, were obtained from the mother liquor either upon its concentration under vacuum followed by addition of Et$_2$O or by taking the solution to dryness followed by recrystallization of the residue from thf/Et$_2$O (typically ca. 30−60% yields for the pure isomers, with the higher values for the products with electron-withdrawing substituents of the aromatic nitrile ring, **2e** and **2f**). Total yields (**1** + **2**): ca. 60−80%.

As an example of this general procedure, *cis*- and *trans*-[ReCl{NC(H)C$_6$H$_4$OMe-4}(dppe)$_2$][BF$_4$], **1b** and **2b**, were prepared as follows:

cis-[ReCl(NCC$_6$H$_4$OMe-4)(dppe)$_2$] (0.37 g, 0.32 mmol) was dissolved in dichloromethane (20 cm^3), and a 5-fold molar excess of HBF$_4$/Et$_2$O solution (3.0 cm^3, 1.6 mmol; see above) was added. The color of the solution turned from the initial red to brownish yellow (upon the addition of the first equimolar amount of the acid) and finally to green. The system was left stirring for 1 h. The solution was then concentrated under vacuum, and after addition of Et$_2$O it was left standing overnight. The nonhomogeneous solid thus precipitated was filtered off and consisted of aggregates of yellow crystals of *cis*-[ReCl{NC(H)C$_6$H$_4$OMe-4}(dppe)$_2$][BF$_4$] **1b** together with yellow needle crystals of *trans*-[ReCl$_2$(dppe)$_2$]. After mechanical separation of the **1b** aggregates, they were washed with a mixture of CH$_2$Cl$_2$/Et$_2$O (1:3) and dried under vacuum (ca. 0.18 g, 40% yield). The mother liquor was taken to dryness and the residue recrystallized from thf/Et$_2$O thus leading to the precipitation of the methyleneamide compound *trans*-[ReCl{NC(H)C$_6$H$_4$OMe-4}(dppe)$_2$][BF$_4$] **2b**, in a pure form, which was filtered off and dried under vacuum (ca. 0.13 g, 30% yield).

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Alternatively, complexes **2** can be synthesized by protonation of the corresponding *trans*-[ReCl(NCC$_6$H$_4$X-4)(dppe)$_2$] **3**, in CH_2Cl_2, on addition of the acid, HBF_4/Et_2O solution, in a stoichiometric amount. The yield of this protonation step is nearly quantitative, but the procedure requires the previous synthesis of **3** (see below).

1b: yellow solid. ^{1}H NMR (d_6-acetone): δ 7.80−6.85 (m, 40H, Ph dppe), 6.79 (d, 2H, $^3J_{HH}$ = 8.7 Hz, Ph methyleneamide), 6.39 (d, 2H, $^3J_{HH}$ = 8.7 Hz, Ph methyleneamide), 3.88 (s, 3H, CH_3), 3.35 (m, 1H, CH_2), 3.20−2.98 (m, br, 3H, CH_2), 2.58−2.26 (m, br, 3H, CH_2), 2.18 (m, 1H, CH_2), −7.11 (m, 1H, J_{AX} = 14.2 Hz, J_{BX} = 37.8 Hz, J_{CX} = 45.7 Hz, J_{DX} = 60.1 Hz, N=C*H*R). ^{31}P{^{1}H} NMR (d_6-acetone): δ_A −130.24, δ_B −127.11, δ_C −117.03, δ_D −106.62; J_{AB} = 17.0 Hz, J_{AC} = 199.0 Hz, J_{AD} = 5.8 Hz, J_{BC} = 4.2 Hz, J_{BD} = 12.0 Hz, J_{CD} = 11.8 Hz. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 163.15 (s, C_p methyleneamide), 140.92−125.64 (m, Ph), 113.85 (s, N*C*HR), 100.54 (s, C_i methyleneamide), 55.13 (s, *C*H$_3$), 32.15 (dd, ^1J = 36.4 Hz, ^2J = 10.1 Hz, *C*H$_2$), 30.15 (dd, ^1J = 32.5 Hz, ^2J = 11.4 Hz, *C*H$_2$), 27.96 (dd, ^1J = 31.4 Hz, ^2J = 8.2 Hz, *C*H$_2$), 26.69 (dd, ^1J = 32.9 Hz, ^2J = 4.5 Hz, *C*H$_2$).^{13}C NMR (CD_2Cl_2): δ 163.15 (s, br), 140.92−125.64 (m), 113.85 (d, $^1J_{CH}$ = 164.3 Hz), 100.54 (t, $^2J_{CH}$ = 9.3 Hz), 55.13 (q, $^1J_{CH}$ = 146.5 Hz), 32.15 (m), 30.15 (m), 27.96 (m), 26.69 (m). Anal. Calcd for $H_{56}BC_{60}NOF_4ClP_4Re\cdot{}^1/_2CH_2Cl_2$: C, 56.7; H, 4.5; N, 1.1. Found: C, 56.2; H, 4.5; N, 1.1. FAB$^+$-MS: *m*/*z* 1116 [M − Cl]$^+$ (M$^+$, calcd 1151), 1019 [M − NCHR]$^+$, 753 [M − dppe]$^+$.

1c: yellow solid. ^{1}H NMR (d_6-acetone): δ 7.70−6.89 (m, 40H, Ph), 6.92 (t, $^3J_{HH} \approx {}^3J_{HP} \approx$ 8.6 Hz, 2H, H_o dppe), 6.34 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ph methyleneamide), 3.22 (m, 1H, CH_2), 3.10−2.78 (m, br, 3H, CH_2), 2.63−2.28 (m, br, 3H, CH_2) 2.20 (m, 1H, CH_2) 2.40 (s, 3H, CH_3), −7.20 (m, 1H, J_{AX} = 14.4 Hz, J_{BX} = 37.0 Hz, J_{CX} = 46.2 Hz, J_{DX} = 59.7 Hz, N=C*H*R). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_A −114.27, δ_B −103.23, δ_C −112.40, δ_D −91.74; J_{AB} = 8.1 Hz, J_{AC} = 198.1 Hz, J_{AD} = 17.1 Hz, J_{BC} = 5.6 Hz, J_{BD} = 16.0 Hz, J_{CD} = 10.5 Hz. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 149.27 (s, C_m methyleneamide), 146.05 (s, C_p methyleneamide), 142.23 (s, C_o methyleneamide), 137.3−125.3 (m, Ph-dppe), 123.07 (s, N*C*HR), 107.16 (s, C_i methyleneamide), 33.31 (dd, ^1J = 36.0 Hz, ^2J = 8.7 Hz, *C*H$_2$), 30.89 (dd, ^1J = 34.9 Hz, ^2J = 8.7 Hz, *C*H$_2$), 28.16 (dd, ^1J = 31.0 Hz, ^2J = 8.7 Hz, *C*H$_2$), 27.41 (dm, ^1J = 32.3 Hz, *C*H$_2$), 22.03 (s, *C*H$_3$). ^{13}C NMR (CD_2Cl_2): δ 149.27 (d, $^1J_{CH}$ = 158.6 Hz), 146.05 (s, br), 142.23 (d, $^1J_{CH}$ = 160.8 Hz), 137.3−125.3 (m, br), 123.07 (d, br, $^1J_{CH}$ = 160.0 Hz), 107.16 (t, ^2J = 7.3 Hz), 33.31 (m), 30.89 (m), 28.16 (m), 27.41 (m), 22.03 (q, $^1J_{CH}$ = 127.8 Hz). Anal. Calcd for $H_{56}BC_{60}NF_4ClP_4Re$: C, 58.9; H, 4.6; N, 1.1. Found: C, 59.1; H, 4.8; N, 1.2. FAB$^+$-MS: *m*/*z* 1136 [M]$^+$, 1100 [M − Cl]$^+$, 1019 [M − NCHR]$^+$,

1d: yellow solid. ^{1}H NMR (d_6-acetone): δ 7.67−6.90 (m, 43H, Ph), 6.46 (d, $^3J_{HH}$ = 7.3 Hz, 2H, H_o methyleneamide), 3.55 (m, 1H, CH_2), 3.10−2.80 (m, br, 3H, CH_2), 2.63−2.35 (m, br, 3H, CH_2), 2.10 (m, 1H, CH_2), −7.28 (m, 1H, J_{AX} = 14.2 Hz, J_{BX} = 39.0 Hz, J_{CX} = 43.6 Hz, J_{DX} = 60.1 Hz, N=C*H*R). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_A −124.46, δ_B −127.69, δ_C −117.61, δ_D −98.27; J_{AB} = 16.0 Hz, J_{AC} = 194.8 Hz, J_{AD} = 12.8 Hz, J_{BC} = 0.5 Hz, J_{BD} = 11.6 Hz, J_{CD} = 10.6 Hz. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 149.97 (s, C_m methyleneamide), 142.71 (s, C_o methyleneamide), 140.1−125.2 (m, Ph-dppe + C_p methyleneamide), 123.48 (s, N*C*HR), 110.77 (s, C_i methyleneamide), 33.46 (dd, ^1J = 36.3 Hz, ^2J = 10.6 Hz, *C*H$_2$), 30.85 (dd, ^1J = 44.4 Hz, ^2J = 12.0 Hz, *C*H$_2$), 28.16 (dd, ^1J = 31.4 Hz, ^2J = 9.6 Hz, *C*H$_2$), 27.35 (dd, ^1J = 28.5 Hz, ^2J = 3.4 Hz, *C*H$_2$). ^{13}C NMR (CD_2Cl_2): δ 149.97 (d, br, $^1J_{CH}$ = 160.6 Hz), 142.71 (d, br, $^1J_{CH}$ = 157.9 Hz), 140.1−125.2 (m), 123.48 (d, br, $^1J_{CH}$ = 165.0 Hz), 110.77 (s, br), 33.46 (m), 30.85 (m), 28.16 (m), 27.35 (m). Anal. Calcd for $H_{54}BC_{59}NF_4ClP_4Re\cdot 2CH_2Cl_2$: C, 53.1; H, 4.2; N, 1.0. Found: C, 53.7; H, 3.6; N, 0.8.

1e: yellow solid. ^{1}H NMR (d_6-acetone): δ 7.97−6.95 (m, 44H, Ph), 3.50−2.62 (m, br, 8H, CH_2 dppe), −6.80 to −7.33 (m, 1H, NC*H*R). ^{19}F NMR (d_6-acetone): δ −149.8 (m, methyleneamide), −154.0 (s, BF_4). Not analytically pure.

1f: yellow solid. ^{1}H NMR (CD_2Cl_2): δ 7.64−6.96 (m, 40H, Ph dppe), 6.91 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph methyleneamide), 6.38 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph methyleneamide), 3.18 (m, 1H, CH_2), 3.10−2.78 (m, br, 3H, CH_2), 2.68−2.40 (m, br, 3H, CH_2), 2.18 (m, br, 1H, CH_2), −7.02 (m, 1H, J_{AX} = 13.9 Hz, J_{BX} = 36.4 Hz, J_{CX} = 45.9 Hz, J_{DX} = 60.4 Hz, N=C*H*R). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_A −127.83, δ_B −127.30, δ_C −116.09, δ_D −103.04; J_{AB} = 8.2 Hz, J_{AC} = 195.9 Hz, J_{AD} = 8.5 Hz, J_{BC} = 1.1 Hz, J_{BD} = 9.9 Hz, J_{CD} = 12.2 Hz. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 149.58 (s, C_m methyleneamide), 142.21 (s, C_o methyleneamide), 141.01 (s, C_p methyleneamide), 137.7−127.6 (m, Ph dppe), 123.18 (s, N*C*HR), 108.83 (s, C_i methyleneamide), 33.44 (dd, ^1J = 30.2 Hz, ^2J = 9.2 Hz, *C*H$_2$), 30.79 (dd, ^1J = 33.9 Hz, ^2J = 10.4 Hz, *C*H$_2$), 28.06 (dd, ^1J = 31.9 Hz, ^2J = 8.9 Hz, *C*H$_2$), 27.29 (dd, ^1J = 32.4 Hz, ^2J = 4.6 Hz, *C*H$_2$). ^{13}C NMR (CD_2Cl_2): δ 149.58 (d, $^1J_{CH}$ = 160.6 Hz), 142.21 ($^1J_{CH}$ = 162.9 Hz, ^2J = 6.6 Hz), 141.01 (s, br), 137.70−127.60 (m), 123.18 (d, $^1J_{CH}$ = 166.0 Hz), 108.83 (t, ^2J = 8.9 Hz), 33.44 (m), 30.79 (m), 28.06 (m), 27.29 (m). Anal. Calcd for $H_{52}BC_{59}NF_5Cl_2P_4Re\cdot{}^1/_2CH_2Cl_2$: C, 54.9; H, 4.2; N, 1.1. Found: C, 54.6; H, 4.8; N, 1.1. FAB$^+$-MS: *m*/*z* 1155 [M]$^+$, 1119 [M − Cl]$^+$, 1019 [M − NCHR]$^+$.

2a: greenish yellow. ^{1}H NMR (CD_2Cl_2): δ 7.45−7.04 (m, 42H, Ph), 5.25 (d, $^3J_{HH}$ = 6.8 Hz, 2H, H_o methyleneamide), 3.68−3.40 (m, br, 4H, CH_2 methyleneamide), 2.92 (m, br, 4H, CH_2 dppe), 2.76 (m, br, 4H, CH_2 dppe), 1.12 (t, $^3J_{HH}$ = 6.7 Hz, 6H, CH_3), −3.81 (qt, $^4J_{HP}$ = 6.1 Hz, 1H, N=C*H*R). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −132.85. ^{13}C NMR (CD_2Cl_2): δ 153.55 (s, Ph), 136.09−119.0 (m, Ph), 33.57−28.81 (m, *C*H$_2$), 11.72 (q, $^1J_{CH}$ = 131.6 Hz, *C*H$_3$). Anal. Calcd for $H_{63}BC_{63}N_2F_4ClP_4Re\cdot{}^1/_2CH_2Cl_2$: C, 55.0; H, 4.7; N, 2.0. Found: C, 54.8; H, 4.9; N, 2.4.

2b: yellow. ^{1}H NMR (CD_2Cl_2): δ 7.50−6.54 (m, 40H, Ph), 6.15 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H_m methyleneamide), 5.18 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H_o methyleneamide), 3.81 (s, 3H, CH_3), 2.91 (m, br, 4H, CH_2 dppe), 2.71 (m, br, 4H, CH_2 dppe), −4.82 (qt, $^4J_{HP}$ = 6.6 Hz, 1H, N=C*H*R).^{31}P{^{1}H} NMR (CD_2Cl_2): δ −130.44. Anal. Calcd for $H_{56}BC_{60}NOF_4ClP_4Re$: C, 58.1; H 4.6; N 1.1. Found: C, 57.8; H, 4.8; N, 1.3. FAB$^+$-MS: *m*/*z* 1152 [M]$^+$, 1019 [M − NCR]$^+$, 982 [M − NCR − Cl]$^+$.

2d: yellow. ^{1}H (CD_2Cl_2) NMR: δ 7.36−6.94 (m, 40H, Ph dppe), 6.87 (t, $^3J_{HH}$ = 7.7 Hz, 3H, H_m + H_p methyleneamide), 5.15 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H_o methyleneamide), 2.82 (m, br, 4H, CH_2), 2.53 (m, br, 4H, CH_2), −4.74 (qt, $^4J_{HP}$ = 6.8 Hz, 1H, N=C*H*R). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −130.50. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 149.64 (br, Ph), 142.28 (s, Ph), 134.01 (d, J_{CP} = 22.3 Hz, Ph), 131.34 (d, J_{CP} = 22.3 Hz, Ph), 129.00 (d, J_{CP} = 17.8 Hz, Ph), 123.12 (s, br, N=*C*HR) 30.00 (m, br, *C*H$_2$). ^{13}C (CD_2Cl_2): δ 149.64 (d, br, ^1J = 161.9 Hz), 142.28 (d, br, $^1J_{CH}$ = 161.9 Hz), 134.01 (dm, $^1J_{CH}$ = 161.0 Hz), 129.00 (dd, $^1J_{CH}$ = 159.4 Hz), 123.12 (d, br, $^1J_{CH}$ = 151.3 Hz), 30.00 (tm, br, $^1J_{CH}$ = 117.7 Hz). Anal. Calcd for $H_{54}BC_{59}NF_4ClP_4Re\cdot{}^1/_2CH_2Cl_2$: C, 57.1; H, 4.4; N, 1.1. Found: C, 56.9; H, 4.8; N, 1.1.

2e: yellow. ^{1}H NMR (CD_2Cl_2): δ 7.33−6.99 (m, 40H, Ph), 6.56 (t, $^3J_{HH} \approx {}^3J_{HF}$ = 8.7 Hz, 2H, H_m methyleneamide), 5.06 (dd, $^2J_{HH}$ = 8.7 Hz, $^4J_{HF}$ = 5.1 Hz, 2H, H_o methyleneamide), 2.81 (m, br, 4H, CH_2), 2.68 (m, br, 4H, CH_2), −4.71 (qt, $^4J_{HP}$ = 6.4 Hz, 1H, N=C*H*R). ^{19}F NMR (d_6-acetone): δ −114.1 (tt, ^3J = 9.0 Hz, ^4J = 4.9 Hz). ^{31}P{^{1}H} (CD_2Cl_2) NMR: δ −130.77. ^{13}C{^{1}H} NMR (CD_2-

Cl_2): δ 149.59 (s, br, Ph), 142.24 (s, Ph), 137.57 (s, Ph), 134.01 (d, J_{CP} = 24.8 Hz, Ph), 131.39 (d, J_{CP} = 23.5 Hz, Ph), 130.37−129.29 (m, br, Ph), 128.95 (d, J_{CP} = 34.8 Hz, Ph), 128.49 (s, N*C*HR), 125.57 (s, Ph), 123.15 (s, Ph), 114.32 (d, $^2J_{CF}$ = 21.65 Hz, C_m methyleneamide), 110.77 (s, br, C_i methyleneamide), 30.24 (qt, J_{CP} = 10.6 Hz, *C*H_2).^{13}C (CD_2Cl_2): δ 149.59 (d, br, $^1J_{CH}$ = 164.4 Hz), 142.24 (d, br, $^1J_{CH}$ = 162.5 Hz), 137.57 (d, br, $^1J_{CH}$ = 176.1 Hz), 134.01 (dd, J_{CH} = 164.4 Hz), 128.95 (dd, $^1J_{CH}$ = 162.8 Hz), 125.57 (d, br, $^1J_{CH}$ = 166.3 Hz), 123.15 (d, br, $^1J_{CH}$ = 162.5 Hz), 114.32 (d, br, $^1J_{CH}$ = 163.7 Hz), 110.77 (s, br), 30.24 (tm, $^1J_{CH}$ = 130.9 Hz). Anal. Calcd for $H_{53}BC_{59}NF_5ClP_4Re\cdot 2CH_2Cl_2$: C, 52.4; H, 4.1; N, 1.0. Found: C, 52.4; H, 4.5; N, 1.2.

2f: yellow. ^{1}H NMR (CD_2Cl_2): δ 7.77−6.98 (m, 40H, Ph-dppe), 6.80 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_m methyleneamide), 4.98 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H_o methyleneamide), 2.80 (m, br, 4H, C*H*$_2$), 2.61 (m, br, 4H, C*H*$_2$), −4.68 (qt, $^4J_{HP}$ = 6.3 Hz, 1H, N=C*H*R).^{31}P{^{1}H} NMR: δ −130.11. ^{13}C{^{1}H} (CD_2Cl_2): δ 149.70 (s, br, C_p methyleneamide), 142.30 (s, C_m methyleneamide), 136.92 (s, C_o methyleneamide), 133.97 (d, J_{CP} = 23.5, Ph), 131.43 (d, J_{CP} = 24.8, Ph), 130.12−129.51 (m, Ph), 128.97 (d, J_{CP} = 34.1 Hz, Ph), 127.33 (s, N=*C*HR), 113.81 (s, C_i methyleneamide), 30.20 (qt, J_{CP} = 11.0 Hz, *C*H_2).^{13}C NMR: δ 149.70 (s, br), 142.30 (d, br, $^1J_{CH}$ = 164.5 Hz), 136.92 (d, $^1J_{CH}$ = 175.8 Hz), 133.97 (dd, $^1J_{CH}$ = 161.3 Hz, Ph), 128.97 (dd, $^1J_{CH}$ = 162.5 Hz), 127.33 (d, $^1J_{CH}$ = 164.4 Hz), 113.81 (t, ^2J = 7.5 Hz), 30.20 (tm, $^1J_{CH}$ = 137.7 Hz). Anal. Calcd for $H_{52}BC_{59}NF_5Cl_2P_4Re$: C, 56.9; H, 4.3; N, 1.1. Found: C, 56.4; H, 4.7; N, 1.0. FAB$^+$-MS: *m*/*z* 1157 [M]$^+$, 1019 [M − NCR]$^+$, 758 [M − dppe]$^+$.

Synthesis of *cis*-[ReCl{NC(SiMe$_3$)C$_6$H$_4$Me-4}(dppe)$_2$][CF$_3$SO$_3$], 1c′. A thf (20 cm^3) suspension of *cis*-[ReCl(NCC$_6$H$_4$Me-4)(dppe)$_2$] (0.23 g, 0.20 mmol) was kept at low temperature (−63.5 °C, by means of a cryostatic $CHCl_3$/liquid N_2 bath), and a slight (1.5:1) molar excess of $SiMe_3CF_3SO_3$ (0.060 cm^3, 0.31 mmol) in thf (5 cm^3) was added dropwise. The solution changed from yellow to the final red color upon gradual raising of the temperature. By concentration of the solution and addition of Et_2O a pale yellow solid was formed, which was filtered off, washed with a 1:3 mixture of thf:Et_2O and then with Et_2O, and dried under vacuum (0.19 g, 70% yield). Further crops precipitated from the mother liquor contained the dinitrile complex *cis*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$][CF$_3$SO$_3$].

1c′: pale yellow solid. ^{1}H NMR ($CDCl_3$): δ 7.43−6.91 (m, 40H, Ph dppe + methyleneamide), 6.83 (t, $^3J_{HH} \approx {}^3J_{HP} \approx$ 8.7 Hz, 2H, H_m Ph dppe), 6.25 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ph methyleneamide), 3.18 (m, 1H, C*H*$_2$), 3.05−2.68 (m, br, 3H, C*H*$_2$), 2.55−2.28 (m, br, 3H, C*H*$_2$), 2.10 (m, 1H, C*H*$_2$), 2.31 (s, 3H, C*H*$_3$), 1.47 (m, br, 9H, Si(C*H*$_3$)$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ_A −124.44, δ_B −126.41, δ_C −116.93, δ_D −98.16; J_{AB} = 18.5 Hz, J_{AC} = 195.3 Hz, J_{AD} = 12.2 Hz, J_{BC} = 2.5 Hz, J_{BD} = 12.2 Hz, J_{CD} = 9.1 Hz. Anal. Calcd for $H_{64}C_{64}NO_3F_3SClSiP_4Re$: C, 56.6; H, 4.8; N, 1.0. Found: C, 56.8; H, 4.5; N, 1.1. FAB$^+$-MS: *m*/*z* 1019 [M − NCHR − SiMe$_3$]$^+$ (M$^+$, calcd 1212). During the time scale required for ^{13}C NMR data acquisition, the complex underwent hydrolysis to **1c**.

Syntheses of *trans*-[ReCl(NCC$_6$H$_4$X-4)(dppe)$_2$] [X = NEt$_2$ (3a), OMe (3b), H (3d), F(3e), or Cl (3f)]. These compounds can be obtained[24] directly from the rhenium−dinitrogen complex *trans*-[ReCl(N$_2$)(dppe)$_2$], but they are then contaminated with the corresponding cis isomers which constitute the main products. A more convenient method, with almost quantitative yields, consists of the deprotonation of complexes **1** or **2**. The general procedure is described for *trans*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$], **3e**, as follows:

To a dichloromethane solution (5 cm^3) of *trans*-[ReCl{NC(H)-C$_6$H$_4$F-4}(dppe)$_2$][BF$_4$] **2e** (or **1e**) (0.11 g, 0.09 mmol) was added dropwise a slight molar excess of a 0.10 M alcoholic solution of [NBu$_4$][OH] (1.34 cm^3, 0.13 mmol). The yellow reaction solution of **2e** turned to deep red. After stirring for 5 min the solution was concentrated under vacuum and Et_2O was added; this procedure had to be repeated 4−5 times until **3e** precipitated as a microcrystalline red solid, which was filtered off, washed with a 1:3 mixture of CH_2Cl_2/Et_2O and then with Et_2O, and dried under vacuum (0.095 g, 90% yield).

3a: orange solid. IR (KBr pellet): 2111 s (ν$_{N≡C}$). ^{1}H NMR (C_6D_6): δ 7.67−6.42 (m, 44H, Ph), 2.53 (s, br, 4H, C*H*$_2$, nitrile), 2.19 (s, br, 4H, C*H*$_2$), 1.97 (s, br, 4H, C*H*$_2$), 0,37 (t, $^3J_{HH}$ = 7.1 Hz, 6H, C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ −111.6. Not analytically pure.

3b: red solid. IR (KBr pellet): 2090 s (ν$_{N≡C}$). ^{1}H NMR (C_6D_6): δ 7.27−7.07 (m, 40H, Ph dppe), 6.74 (d, $^3J_{HH}$ = 8.7 Hz, 2H, Ph nitrile), 6.26 (d, $^3J_{HH}$ = 8.7 Hz, 2H, Ph nitrile), 2.90 (s, br, 4H, C*H*$_2$), 2.67 (s, br, 4H, C*H*$_2$), 2.53 (s, 3H, C*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ −111.9. Anal. Calcd for $H_{55}C_{60}NOClP_4Re$: C, 62.6; H, 4.8; N, 1.3. Found: C, 64,7; H, 4,9; N, 1.5. FAB$^+$-MS: *m*/*z* 1151 [M]$^+$, 1019 [M − NCR]$^+$.

3d: dark red solid. IR (KBr pellet) 2080 s (ν$_{N≡C}$). ^{1}H NMR (C_6D_6): δ 8.20−7.05 (m, 45H, Ph), 2.59 (s, br, 4H, C*H*$_2$), 2.35 (s, br, 4H, C*H*$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ −114.1. Not analytically pure.

3e: dark red solid. IR (KBr pellet): 2100 s (ν$_{N≡C}$). ^{1}H NMR (CD_2Cl_2): δ 7.94−6.76 (m, 44H, Ph), 2.59 (s, br, 4H, C*H*$_2$), 2.35 (s, br, 4H, C*H*$_2$).^{19}F NMR (CD_2Cl_2): δ −106.2 (br). ^{31}P{^{1}H} NMR [at −5 °C in a mixture of 4:1 thf/$(CD_3)_2CO$]: δ −112.1. Anal. Calcd for $H_{52}C_{59}NFClP_4Re\cdot{}^1/_8CH_2Cl_2$: C, 61.7; H, 4.6; N, 1.2. Found: C, 62.2; H, 4.6; N, 1.2.

3f: dark red solid. IR (KBr pellet): 2080 s (ν$_{N≡C}$). ^{1}H NMR (CD_2Cl_2): δ 8.20−6.70 (m, 44H, Ph), 2.83 (s, br, 4H, C*H*$_2$), 2.59 (s, br, 4H, C*H*$_2$). ^{31}P{^{1}H} NMR: δ −112.9. Anal. Calcd for $H_{52}C_{59}NCl_2P_4Re$: C, 61.3; H, 4.5; N, 1.2. Found: C, 60.8; H, 4.8; N, 1.3.

Syntheses of *trans*-[ReCl(NCC$_6$H$_4$X-4)(dppe)$_2$][PF$_6$] [X = Me (4c), H (4d), or Cl (4f)]. The general procedure (ca. 70−80% yields) is illustrated for *trans*-[ReCl(NCC$_6$H$_4$Cl-4)(dppe)$_2$][PF$_6$] **4f** as follows:

To a dichloromethane solution (20 cm^3) of *cis*-[ReCl(NCC$_6$H$_4$-Cl-4)(dppe)$_2$] (0.27 g, 0.23 mmol), kept at ca. −63 °C in a cryostatic mixture of $CHCl_3$/liquid N_2, was added an excess of [Et$_3$O][PF$_6$] (0.14 g, 0.55 mmol) with stirring. By gradually increasing the temperature, the initially red solution slowly became orange. Upon successive evaporations of the solvent and additions of Et_2O, three fractions of **4f** were obtained, which were all gathered and recrystallized from CH_2Cl_2/Et_2O. The obtained orange crystals were isolated by filtration, washed with Et_2O, and dried under vacuum (0.23 g, 75% yield). Compounds **4** are paramagnetic.

4c:[39] orange-yellow solid. IR: 2130 m (ν$_{N≡C}$). Anal. Calcd for $H_{55}C_{60}NF_6P_5ClRe$: C, 56.3; H, 4.3; N, 1.1. Found: C, 57.5; H, 4.7; N, 1.3. FAB$^+$-MS: *m*/*z* 1134 [M]$^+$, 1019 [M − NCR]$^+$.

4d: yellow solid. IR: 2130 m (ν$_{N≡C}$). Anal. Calcd. for $H_{53}C_{59}NF_6P_5ClRe.1CH_2Cl_2$: C, 53.3; H, 4.1; N, 1.0. Found: C, 53.1; H, 4.2; N, 1.2.

4f: orange solid. IR: 2120 m (ν$_{N≡C}$). Anal. Calcd for $H_{52}C_{59}NF_6P_5Cl_2Re\cdot CH_2Cl_2$: C, 52.0; H, 3.9; N, 1.0. Found: C, 52.4; H, 3.8; N, 1.0. FAB$^+$-MS: *m*/*z* 1155 [M]$^+$, 1019 [M − NCR]$^+$.

X-ray Crystallography. Crystal data for *trans*-[ReCl{NC(H)-C$_6$H$_4$F-4}(dppe)$_2$][BF$_4$]·CH$_2$Cl$_2$. $C_{60}H_{55}BCl_3F_5NP_4Re$, M = 1312.37, triclinic, space group $P\bar{1}$, a = 12.881(3) Å, b = 14.767(3) Å, c = 17.785(4) Å, α = 84.55(2)°, β = 74.64(2)°, γ = 65.82(2)°, V = 2975.6(13) Å^3, T = 293 K, Z = 2, μ(Mo Kα) = 2.3 mm^{-1}. Cell

dimensions were obtained from 10951 reflections measured, 10440 independent ($R_{int} = 0.0526$). Final wR(F^2) = 0.1902, R1 = 0.0669. Intensity data were collected using an Enraf-Nonius CAD4 diffractometer in the range 1.5−25.0° with index ranges $-15 \le h \le 0$, $-17 \le k \le 16$, $-21 \le l \le 20$. Structure was solved by direct methods by using the SHELXS-86 program[45] and refined with SHELXL-97.[46] The maximum and minimum peaks in the final difference electron density map are of 2.85 and −2.06 e Å^{-3} located in the immediate vicinity of the rhenium atom and close to one of the positions of the CH_2Cl_2 molecule of solvation.

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Acknowledgment. The work has been partially supported by the PRAXIS XXI Program and the Fundação para a Ciência e a Tecnologia (FCT). We are also indebted to Prof. Raymond L. Richards (University of Sussex) for stimulating discussions, as well as to Dr. Adelino Galvão and Prof. Teresa Duarte (Centro de Química Estrutural, Lisbon) for their advice on the X-ray structural analysis.

Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010841M